

Mineralogy and genesis of soils developed from ultrabasic and alkaline rocks of Lages Alkaline Complex, Brazil

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ABSTRACT: In the Plateau of Lages, intrusions of alkaline and ultrabasic rocks occur, rocks of rare occurrence in Brazil, whose soils derived from them are practically unknown. The study aimed to evaluate the chemical composition, mineralogy, genesis, and classification of the soils developed from the rocks Nepheline Sienite (P1), Volcanic Breccia (P2), Kimberlitic Breccia (P3), Phonolitic Tephrite (P4), and Phonolite (P5). After the morphological description (field) and the collection of soil samples, chemical analyses of the soils, mineralogical of the clay fraction and the total elements of the soils and the corresponding rocks that gave rise to them were carried out. Three Humudepts (Cambissolos), a Hapludolls (Chernossolo), and a Kandiudox (Nitossolo) were identified. Except for the P3 profile, the others are acidic soils, with high levels of exchangeable aluminum, poor in basic cations, with low sum and base saturation, showing a high degree of weathering and strong leaching. In the clay fraction, the presence of 2:1 clay minerals predominated with kaolinite with interlayered hydroxy-Al polymers. The P3 profile showed a slightly acidic reaction, high sum and base saturation, and practically zero exchangeable aluminum, a situation compatible with mineralogy, where trioctahedral vermiculite predominated, revealing that it was a young, slightly weathered soil.

Key words: chemical properties; genesis; mineralogy; soils derived from alkaline and ultrabasic rocks

Mineralogia e gênese de solos desenvolvidos de rochas alcalinas e ultrabásicas do Complexo Alcalino de Lages, Brasil

RESUMO: No Planalto de Lages, ocorrem intrusões de rochas alcalinas e ultrabásicas, rochas de rara ocorrência no Brasil, cujos solos delas derivados são praticamente desconhecidos. O estudo objetivou avaliar a composição química, a mineralogia, a gênese e a classificação dos solos desenvolvidos das rochas Nefelina Sienito (P1), Brecha Vulcânica (P2), Brecha Kimberlítica (P3), Tefrito Fonolítico (P4) e Fonolito (P5). Para isso, após a descrição morfológica (campo) e a coleta de amostras de solos, procedeu-se as análises químicas dos solos, mineralógicas da fração argila e dos elementos totais dos solos e das rochas correspondentes que lhes deram origem. Foram identificados três Cambissolos, um Chernossolo e um Nitossolo. Com exceção do perfil P3, os demais são solos ácidos, com elevados teores de alumínio trocável, pobres em cátions básicos, com baixa soma e saturação por bases, evidenciando alto grau de intemperismo e forte lixiviação. Na fração argila predominou a caulinita a presença de argilominerais 2:1 com polímeros hidroxi-Al entrecamadas. O perfil P3 apresentou reação ligeiramente ácida, elevada soma e saturação por bases, e alumínio trocável praticamente nulo, situação compatível com a mineralogia, onde predominou a vermiculita trioctaedral, revelando tratar-se de um solo jovem, pouco intemperizado.

Palavras-chave: propriedades químicas; gênese; mineralogia; solos derivados de rochas alcalinas e ultrabásicas

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Introduction

In the region of Plateau of Lages, SC, lies the Lages Alkaline Complex (Complexo Alcalino de Lages) (CPRM, 2014), a formation composed of intrusions of alkaline and ultrabasic rocks. Although they occupy a small geographic extension, the rocks in the complex are described by Scheibe (1986) as peculiar, with great lithological diversity, where phonolites, nepheline syenites, olivine-melilithites, lamprophyres, in addition to carbonatites, kimberlites, and breccia pipe stand out (Machado et al., 2012).

Characteristics of soils developed from rocks derived from the lava flow from the Serra Geral Formation and Gondwana sedimentary rocks, dominant in the region, are reasonably well known (Ferreira, 2013; Teske et al., 2013). However, for rocks developed from the Lages Alkaline Complex, there is a single study conducted by Ferreira (2013), in which soils derived from phonolite, syenite, and olivine melilithite were studied.

Almeida et al. (2019) mainly identified Cambissolos Húmicos e Háplicos derived from Gondwana sedimentary rocks, all with strongly acidic reaction and low natural fertility, which presented clay mineralogy dominated by kaolinite, but with variable and expressive proportions of 2:1 clay minerals with hydroxy-Al interlayer polymers, (2:1HE) interstratified, and illites. All had very high levels of exchangeable Al (2.20 to 13 cmol kg⁻¹) and very low sum (0.13 to 2.56 cmol kg⁻¹) and base saturation (3 to 20%). For soils derived from the lava flow rocks of the Serra Geral Formation (basalt and rhyodacites), the mineralogy is generally similar to soils derived from sedimentary rocks, but with lower crystallinity of kaolinites, lower exchangeable Al contents (1.01 to 2.65 cmol, kg⁻¹) and with slightly higher sum (0.13 a 1.02 cmol kg⁻¹) and base saturation (3 to 13%) values (Teske et al. 2013; Ferreira, 2013; Almeida et al., 2019).

Soils derived from syenite and phonolite studied by Ferreira (2013) had similar mineralogy and chemical properties to those developed from basalt and rhyodacites; on the other hand, the ultrabasic olivine melilithite derivatives stood out for their high natural fertility and mineralogy dominated by vermiculites, but they occupy an inexpressive area in the regional context. However, this suggests that rocks of more basic constitution (alkaline, basic, and ultrabasic), occurring in the Alkaline Complex, can originate more fertile soils compared to those originated from tephrite and nepheline syenite rocks, which in their chemical composition may contain lows contents, mainly of calcium and magnesium oxides.

Several occurrences of phonolites, syenites, and nepheline syenites are currently being identified in prospecting work to use these materials as a potential source of nutrients, in the form of rock powders or soil remineralizers, to supply mainly potassium for plants in alternatives processes for agricultural production (Martins et al., 2015, Ribeiro, 2018). Also, other rocks, not yet properly mapped and classified, have been identified in preliminary field studies, such as trachytes, tephrites, volcanic, and kimberlite breccias, of which details of the chemical and mineralogical composition, as well as the characteristics of the soils derived from them are unknown.

Due to the lack of information on the chemical and mineralogical composition of soils developed from rocks of the Lages Alkaline Complex (Ferreira, 2013), this study aimed to evaluate five soil profiles developed from different rocks of the Complex mentioned above, with alkaline, basic, and intermediate, seeking to characterize in detail the aspects of its genesis, chemical properties, and mineralogical composition, as well as proceeding with the classification of these soils by the Brazilian Classification System (Santos et al., 2018)

Materials and Methods

According to Köeppen's classification, the climate of the Lages Plateau region, located in Santa Catarina, is of the Cfb type, humid mesothermal, with cold winter and mild summer, with an average temperature of 16°C and average annual rainfall of 1,500 mm. The altitude ranges from 850 to 950m. The region comprises mixed ombrophilous forest (pine forests), and the phytogeographic classification is of general grasslands associated with subtropical subdeciduous forest and araucaria forest (Santa Catarina, 2015).

The study was carried out with samples of five soil profiles, all developed from rocks of the Lages Alkaline Complex (Nepheline syenite -P1; Kimberlites - P2 and P3); Trachyte – P4, and; Phonolite – P5). The formation comprises alkaline and ultrabasic rocks resulting from late magmatism occurring around 75 Ma BP (Machado et al., 2012). The outcrops of the rocks occur as intrusions amid the Gondwana sedimentary rocks in the vicinity of the Serra Geral Formation escarpments. Also called Domo, or Alkaline District of Lages, this corresponds to a stratigraphic window, where the oldest geological occurrences outcrop at levels similar to the alkaline and ultrabasic, younger ones (Scheibe, 1986; Machado et al., 2012). Such rocks occupy approximately 50 km² but are dispersed over a larger area, approximately 1200 km² (Figure 1). Profiles P1, P2, and P5 were in the lower third of the slope in undulating relief; the P3 profile on top of elevation in soft undulating relief; and the P4 profile in the middle third of the slope in undulating relief.

These soil profiles were selected based on different lithologies that occur in the Lages Alkaline Complex, which may have influenced the genesis and properties of the different soils. The identification of rocks in the field and the respective observation sites were made based on the existing geological literature on the region, notably on the maps prepared by Scheibe (1986), Machado et al. (2012) and crossing with approximate geographic coordinates.

A general and morphological description was made for each profile, and samples were collected from the horizons and the underlying rock, carried out in ravines in road cuts, as described in Santos et al. (2015). All environments were under natural vegetation conditions. Afterward, the soil sample collection (deformed) from each horizon identified in the profile was carried out to subsequently carry out chemical,



Source: Machado et al. (2012).

Figure 1. Geological map of the alkaline rocks of the Lages Alkaline Complex, SC.

physical, and mineralogical analyses of the soils. Samples of the underlying rocks were also collected for elemental chemical analyses.

After the collections, the soil samples were dried in a forced circulation oven at 60 °C for 48 hours, chipped with a wooden roller, and sieved in a 2 mm mesh to separate the air-dried fine earth (ADFE). At ADFE, physical, chemical, and mineralogical analyses were performed.

Physical analyses were performed as described in Embrapa (2017), with some adaptations. In summary, 50 g of soil were weighed in a 150 mL snap-cap, then two acrylic pellets and 10 mL of 1 mol L⁻¹ and 75 mL of distilled water were added. Afterward, the samples were stirred on a horizontal stirrer for 4 h at 140 rpm. After this procedure, the samples were washed with fine jets over a 0.053 mm sieve to separate the silt and clay from the sand fraction, quantified by weighing after drying at 105 °C.

To quantify the clay, the Bouyoucus densimeter method (Embrapa, 1979) was used. The sand was quantified gravimetrically after drying at 105 °C, and silt was calculated by difference.

In ADFE, the pH in water and in a KCl 1 mol L⁻¹ solution was determined by potentiometry in a 1:1 ratio. The exchangeable Ca^{2+} , Mg²⁺ e Al³⁺ contents were extracted with a 1 mol L⁻¹ KCl solution. Al³⁺ was quantified by neutralization titration with 0.025 mol L⁻¹ NaOH, using phenolphthalein (2%) as an indicator. Ca^{2+} and Mg²⁺ were determined by atomic absorption spectrophotometry (model: AAnalyst 200 – Perkin Elmer), using lanthanum oxide to control interferents. H+Al was extracted with a 0.5 mol L⁻¹ calcium acetate solution buffered at pH 7.0 and quantified by neutralization titration. K⁺ and Na⁺, extracted by ammonium acetate solution, were quantified by flame photometry. All analyses were performed according to the criteria established in the Soil Analysis Methods Manual (Embrapa, 2017). The total carbon in the soil samples was determined in a Total Carbon Analyzer (TOC) equipment.

Mineralogical analyzes were carried out in the clay fraction, in 2 representative horizons of each profile (P1: horizons B and C1; P2: BAi and C; P3: Bi and Cr; P4: Bt1 and BC e; P5: Bi and C2), by X-ray diffraction. For this, the silt and clay from the particle size analysis were separated by successive decantations based on Stokes' Law (Jackson, 1965). Next, the clay samples were saturated with KCl 1 mol L⁻¹ and MgCl₂ 1 mol L⁻¹ solutions separately. Subsequently, excess salts were eliminated using dialysis bags, submerged in distilled water (DW) with previously measured electrical conductivity (EC). The water change was performed every 3 h until the DW, in which the samples were submerged, reached the initially measured EC (Almeida et al., 2019).

The samples saturated with K⁺ and Mg²⁺ were analyzed in the form of oriented aggregates, and those of K⁺ were read after drying at room temperature, then heated in an oven to read the samples at 110 °C and in the muffle to read the samples at the temperatures of 350 and 550 °C. Those with Mg²⁺ were subjected to air drying (25 °C) and saturation with ethylene glycol vapor (ETG) at 60 °C for 48 h.

Mineralogical analyses were performed using a Philips X-ray diffractometer, model PW 3710, equipped with a copper tube, with a $\theta/2\theta$ compensation angle, vertical goniometer, and a graphite monochromator, with angular variation from 3 to 42 for the samples of oriented clay, with an angular velocity of 0.02 ° 2 θ /s, in step mode, with a reading time of 0.5 seconds per step. To identify the minerals, the parameters of Brown & Brindley (1980), Whittig & Allardice (1986) were used, as well as specific literature indicated in the text, when applicable. For semi-quantification of clay minerals, the

Panalytical X'Pert High Score Plus software (3.0) was used, measuring the relative areas of the main reflections of each identified mineral.

Elemental analyses were performed using the X-ray fluorescence technique, with the elements expressed as oxides. Such analyses were carried out in the clay fraction powder of the selected horizons of each soil profile, previously mentioned, as well as in the rock powder. These analyzes were used to quantify the oxides in the source material of each soil and in the clay fraction to calculate the Ki index, obtained by the formula: Ki = $(SiO_2/Al_2O_3)x1.7$ (Silva, 2020).

The clay fraction and rock samples were ground in an agate mortar until the entire content passed through a 0.053 mm sieve and homogenized. Then, the samples were placed in a cylindrical sampler, with the bottom closed with a polyester film ("mylar") of 3.6 μ m. A compact X-ray fluorescence (XRF) spectrometry equipment, model Epislon 3 from Panalytical was used. To calibrate the equipment, the OMNIAN application (Epsilon software package) was used, which are standard samples in the format of cast pellets, analyzing 24 elements simultaneously.

Results and Discussion

Chemical composition of rocks

The SiO, content evidenced in the phonolite rock powder (P5) was within the expected range (52 to 65%), with a value of 55.11%, placing this rock in the intermediate group. The CaO and MgO contents for this rock are low, totaling 1.86%. On the other hand, those of Na₂O and K₂O are high, as well as those of aluminum. The same interpretation performed for the phonolite can be admited for the nepheline syenite (P1), probably because it is the intrusive correspondent of the phonolite. However, it should be noted that the SiO, contents (51.20%) (Table 1) were slightly below those commonly reported for this rock, classified as intermediate. Then, these results confirm that based on the general composition, the classification of these two rocks as alkaline. Thus, the composition of these two rocks is compatible with the values normally referenced in studies carried out by Scheibe (1986), Le Maitre (2002), and Motoki et al. (2013).

For P2, the elemental composition of the rock collected in this profile shows high SiO_2 content (56.67%) (intermediate group), very low levels of magnesium oxide (0.4%), chromium and strontium, and abnormal aluminum content (Table 1). Nevertheless, it had morphological similarity to kimberlites or kimberlite breccias. Therefore, given the elemental composition observed, it was classified as a volcanic breccia, as also evidenced by Scheibe (1986).

Regarding the rock collected in P3, the elemental composition shows a relatively high content of $SSiO_2$ (47%), high contents of CaO and MgO (sum of these oxides around 22%), titanium, chromium, strontium, and nickel. However, the CaO content exceeded that of MgO (Table 1). Although there was a great morphological similarity between this rock and a kimberlite, it differed from this rock by the higher contents of SiO₂ and MgO and the normal pattern of most kimberlites studied by Costa et al. (1997). Given these results, the rock was classified as a kimberlite breccia.

The chemical composition of the rock collected in P4 has a SiO_2 content of around 49%. Therefore, it belongs to the basic group. Furthermore, this rock has high contents of K, Ca, Al, and P_2O_5 oxides, relatively high Na, and low trace elements. Furthermore, based on the chemical composition data of samples collected in the Lages region by Scheibe (1986) and Aumond & Scheibe (1996), the selected rock would fit better as a porphyritic nepheline syenite. However, for the first author, this rock would be located in the field of phonolitic tephrites. The elementary composition of a tephrite analyzed by Comin-Chiaramonti et al. (2001) in the region of Lages is very similar to the composition of the studied rock.

Similar results regarding the classification of rocks collected in the Lages Alkaline Complex, evidenced in this study, were also verified by Scheibe (1986) and Roldan (2007). After evaluating some rocks from the aforementioned Complex, these authors separated them into leucocratic alkaline (phonolites, porphyritic phonolites, analcime, trachytes, and porphyritic nephelines syenites), alkaline ultrabasic (olivine melilithites and lamprophyres), carbonatites, kimberlites, and volcanic breccias. In addition, the elemental composition of the rocks based on SiO₂ contents are in accordance with those reported by Leinz & Amaral (1985) and Ferreira (2013), although this study found higher levels of basic oxides when compared with those obtained by the last author.

Morphology, physical, and chemical properties of soils

All soils studied, except for P1, showed high levels of carbon in the superficial horizons (Table 2), forming relatively thick and dark A horizons (P1: 49 cm; P2: 40 cm; P3: 25 cm; P4: 60 cm and P5: 38 cm), which can be attributed to the cold and

Table 1. Elements in the form of oxides, by X-Ray fluorescence, of the powder of the rocks of profiles P1 (nepheline syenite), P2 (volcanic breccia), P3 (kimberlite breccia), P4 (trachyte), and P5 (phonolite).

Samula	Na ₂ O	K ₂ O	CaO	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	TiO ₂	Cr ₂ O ₃	NiO	CuO	Sr
Sample	(%)											
P1	2.47	5.08	2.98	1.78	28.48	51.20	0.61	0.64	0.02	0.006	-	0.12
P2	4.30	8.03	1.74	0.41	23.34	56.67	0.40	0.25	0.01	-	-	0.05
P3	-	3.28	17.50	4.74	11.53	47.27	0.99	1.72	0.06	0.06	0.008	0.23
P4	2.47	5.27	6.71	1.33	22.13	48.73	1.30	1.46	-	-	0.003	0.36
P5	-	6.7	1.44	0.42	28.66	55.11	0.51	0.59	0.01	0.001	-	0.04

- not detected

humid climate of the region, which favors its accumulation in the soil (Almeida et al., 2018; 2019). The colors were dark brown and dark grayish brown on this horizon, while on the B horizon, brown and strong brown colors predominated. Except for the P4 profile, the B horizon of the other soils showed little thickness (P1: 110 cm; P2: 103 cm; P3: 80 cm; P4: 150+ and P5: 72 cm) (Table 2), and variations thereof in the lateral extension, a fact that, together with the low textural contrast and absence or low expression of waxiness, indicated the presence of an incipient type B subsuperficial diagnostic horizon.

As for chemical properties, all soils, except for Profile 3, showed acid reaction and low natural fertility, with low pH values in water and KCl 1 mol L^{-1} , low basic cations, and high Al^{3+} and H+Al contents, resulting in high aluminum saturation, being low, therefore, the sum and base saturation, characterizing dystrophic or aluminum soils (Table 2).

The pH in KCl 1 mol L^{-1} was always lower than the pH in water, resulting in a negative net charge balance, which was confirmed by the relatively high values of CEC at pH 7.0, clay fraction activity, and mineralogy of the clay fraction, as shown below. Nevertheless, except for the P3 profile, the other soils

presented clay fraction activity values below 27 cmol_{c} kg⁻¹, characterizing soils with low activity (Tb) (Table 2).

The most acidic profiles, P1, P2, and P5 (compared to the other profiles), had a high exchangeable aluminum content, with an average above 4 cmol_c kg⁻¹, with aluminum saturation above 60%. Conversely, profiles P3 and P4 had lower aluminum values, being inexpressive in P3 (Table 2). Such properties are similar to the vast majority of soils developed from basalt, rhyodacite, and sedimentary rocks occurring in the Planalto Sul Catarinense, verified by several authors (Ferreira, 2013; Teske et al., 2013; Almeida et al., 2019).

In general, the high acidity observed in profiles P1, P2, P4, and P5 (pH ranging from 4.31 to 5.28) can be explained by the constant presence of H⁺ ions from the dissociation of carbonic acid, from the degradation of clay minerals, and the biodegradation of organic matter (OM). In natural environments and a humid climate, with a lack of basic cations, OM's decomposition (biodegradation) is slow. It results in the release of greater amounts of organic acids into the soils, increasing the amounts of H⁺ in the CEC of the soils, increasing even more soil buffering (Lu et al., 2015; Jiang et al., 2018). Therefore, the soil developed from the kimberlite

Table 2. Chemical and physical attributes of soils.

ப (1)	Depth ⁽²⁾	Clay ⁽³⁾	Silt ⁽⁴⁾	Sa. ⁽⁵⁾	TC ⁽⁶⁾	рН (:	l:1)	Al ³⁺	H+AI	Ca ²⁺	Mg ²⁺	K⁺	Na⁺	S ⁽⁷⁾	T ⁽⁸⁾	t ⁽⁹⁾	CA ⁽¹⁰⁾	V ⁽¹¹⁾	m ⁽¹²⁾
п	(cm)		(g ka	g ⁻¹)		Water	KCI					(cmol	kg-1)					(୨	%)
Profile P1 - Nepheline Syenite – Cambissolo Háplico Alumínico típico																			
Α	0-17	520	162	318	14.5	4.72	3.95	4.41	9.64	0	0.063	0.009	0.16	0.23	9.88	4.64	19.00	2	95
AB	17-49	640	126	234	19.3	4.41	3.85	5.87	10.56	0	0.063	0.009	0.18	0.26	10.82	6.13	16.91	2	96
BA	49-61	660	127	213	14.5	4.31	4.05	6.66	10.02	0	0.043	0.008	0.18	0.23	10.26	6.90	15.54	2	96
В	61 -92/95	540	197	263	8.0	4.47	3.92	8.45	11.73	0	0.057	0.012	0.17	0.24	11.97	8.69	22.17	2	97
BC	92/95-110	420	208	372	5.0	4.62	3.83	9.01	12.90	0	0.093	0.022	0.18	0.29	13.20	9.31	31.43	2	97
_C1	110-140	420	188	392	3.7	4.96	4.10	6.33	9.34	0	0.050	0.014	0.16	0.23	9.57	6.57	22.78	2	96
Profile P2 – Volcanic Breccia - Cambissolo Háplico Alumínico típico																			
A1	0-13	420	353	227	33.4	5.28	3.99	2.25	8.17	0.01	0.25	0.87	0.04	1.17	9.34	3.42	22.24	12	66
A2	13-40	520	269	211	20.8	5.25	3.91	3.54	9.18	0.01	0.06	0.99	1.17	2.23	11.41	5.78	21.95	20	61
BAi	40-53/63	560	247	193	12.4	5.02	3.97	4.82	9.0	0.01	0.04	0.32	0.02	0.37	9.37	5.19	16.74	4	93
BC	53/63-103	560	244	196	7.5	5.23	4.03	6.54	12.16	0.01	0.02	0.30	0.09	0.42	12.59	6.97	22.48	3	94
С	82/103-85/95/120	480	300	220	6.6	5.07	3.86	9.97	14.74	0.01	0.04	0.26	0.03	0.65	15.39	10.63	32.06	4	94
CR	85/95/120-160+	340	472	188	3.1	5.16	3.92	10.03	14.97	0.01	0.05	0.36	0.44	0.85	15.83	10.89	46.55	5	92
Profile P3 – Kimberlite Breccia – Chernossolo Háplico Órtico típico																			
A1	0-9	400	355	255	47.7	6.39	4.73	0.06	6.4	7.8	3.86	0.48	0.06	12.19	18.6	11.81	46.60	65	1
A2	9-22/25	400	385	215	47.0	6.95	4.91	0.03	5.6	6.35	4.35	0.18	0.08	10.96	16.57	9.56	41.42	66	0
Bi	22/25-50	440	326	234	20.1	6.66	5.24	0.0	3.85	3.52	6.93	0.22	0.12	10.81	14.66	10.81	33.33	74	0
BC	50-80	440	399	161	8.2	7.5	5.15	0.05	3.27	5.46	16.33	0.36	0.24	22.40	25.68	22.46	58.36	87	0
C1	80-110	420	399	181	6.0	7.11	4.19	0.32	3.69	4.44	18.10	0.42	0.18	24.16	27.85	24.48	66.30	87	1
C2	110-127	400	366	234	3.6	7.05	4.32	0.33	3.33	4.35	17.73	0.29	0.19	22.58	25.91	22.91	64.76	87	1
CR	127-140+	340	376	384	3.4	6.98	4.73	0.11	2.23	4.94	18.67	0.31	0.31	24.25	26.48	24.37	77.90	92	0
				Prof	ile P4 -	- Phono	litic Tep	ohrite -	- Nitosso	lo Brur	no Distro	ófico hú	mico						
A1	0-8/10	500	386	114	59.9	5.23	4.62	0.88	10.26	4.04	0.58	1.10	0.17	5.9	16.16	5.90	32.3	36	15
A2	8/10-36	620	293	87	29.1	5.43	4.42	1.61	9.21	2.29	0.28	0.84	0.15	3.57	12.78	5.18	20.62	28	31
Ae	36-52/60	700	145	55	22.5	5.45	4.0	3.04	10.24	2.55	0.20	0.57	0.15	3.48	13.72	6.53	17.15	25	47
BA	52/60-72/80	720	122	58	14.5	5.43	3.90	3.37	8.42	1.23	0.15	0.38	0.14	1.91	10.33	5.29	12.60	18	64
Bt1	72/80-90/105	740	195	65	10.9	5.58	3.72	3.67	9.04	0.5	0.07	0.24	0.18	1.0	10.04	4.67	13.57	10	79
Bt2	90/105-130	760	165	75	6.5	5.51	3.78	3.93	9.05	0.28	0.06	0.20	0.18	0.72	9.78	4.65	12.86	7	84
BC	130-150+	820	106	74	7.2	5.65	3.83	3.98	9.25	0.33	0.07	0.22	0.15	0.78	10.03	4.77	12.23	8	84
					Profile	P5 - Pho	onolite	– Camb	oissolo H	úmico	Alumíni	co típico)						
A1	0-12	480	421	99	33.3	4.86	3.85	3.94	11.39	1.08	0.10	0.73	0.13	2.06	13.45	6.00	28.02	15	66
A2	12-38	500	408	92	45.9	4.7	3.95	6.05	12.76	0.24	0.14	0.24	0.13	0.77	13.53	6.82	27.07	6	89
Bi	38-52	500	362	138	8.2	4.75	3.72	7.35	12.0	0.016	0.08	0.36	1.07	1.54	13.55	8.90	27.10	11	83
BC	52-72	500	356	144	6.7	4.75	3.80	7.22	10.20	0	0.04	0.29	1.16	1.50	11.71	8.73	23.42	13	83
C1	72-113	480	415	105	4.0	4.80	3.73	6.04	9.18	0	0.02	0.06	0.87	0.96	10.14	7.01	21.13	9	86
C2	113-120+	480	352	168	3.2	4.71	3.88	7.02	10.76	0	0.02	0.08	0.83	0.93	11.70	7.96	24.37	8	88

⁽¹⁾ Horizons collected; ⁽²⁾ Depth; ⁽³⁾ Clay; ⁽⁴⁾ Silt; ⁽⁵⁾ Sand; ⁽⁶⁾ Total carbon; ⁽⁷⁾ Sum of bases; ⁽⁸⁾ CEC at pH7; ⁽⁹⁾ effective CEC; ⁽¹⁰⁾ Clay activity; ⁽¹¹⁾ Base saturation; ⁽¹²⁾ Aluminum saturation.

breccia, compared to the others, is more fertile, with high pH values, basic cation contents, base sum, and saturation and low Al³⁺, H+Al in % (Table 2), similar to the soil derived from olivine melilithite studied by Ferreira (2013) in a relatively close location.

As for the particle size, all soils had a clayey or very clayey texture on the B horizon. The lowest clay contents were observed in the P3 profile (Table 2), developed from kimberlite breccia (Table 1), which presented features of a lower degree of development in field observations, indicated by the expressive presence of phlogopite-type micas in most of the horizons, as will be shown below.

In the P1 and P2 profiles, the Ki value (Table 3) ranged from 2.3 to 2.4 in the B horizon slightly above, therefore, the Ki of kaolinite, this being attributed to the probable presence of 2:1 layer clay minerals in association with kaolinite, which is consistent with the relatively high activity values of the clay fraction (Table 2). At P3, Ki values were around 3.0 to 3.9 for subhorizons B, with an increase in underlying Cr, also suggesting the expressive participation of 2:1 clay minerals in the mineralogical composition of this soil, also being compatible with the high activity values of the clay fraction (Table 2).

Still, in relation to Ki, in P4, it was verified that it was around 2.2 for the main subhorizons of B with a slight increase in the underlying BC. This result suggests the predominance of kaolinite with little participation of clay minerals in the 2:1 layer, such interpretation being consistent with the low clay activity values (Table 2). At P5, the Ki was around 2.6 on the B horizon, confirming the previous idea regarding the likely

Table 3. Ki index determined in the clay and Fe oxide fraction of ADFE by X-Ray Fluorescence, and reflection area around 1.4nm (A14), representative of 2:1 minerals (vermiculite or smectite); at 1.0 nm (A10), from mica or illite; and 0.72nm (A7), from kaolinite, relative to the total areas (At) of these reflections.

Drofile	Horizon	Ki _{XRF}	Fe ₂ O ₃	A ₁₄ /At	A ₁₀ /At	A ₇ /At	
Prome	HUIIZUII	clay	ADFE		°20		
	AB	2.21	7.57	0.24	0.04	0.72	
P1	В	2.27	7.67	0.52	0.07	0.41	
	C1	2.29	7.24	0.41	0.03	0.56	
	A2	2.54	6.34	0.03	0.43	0.42	
20	Bai	2.42	7.22	0.15	0.25	0.60	
٢Z	С	2.39	7.72	0.21	0.19	0.60	
	Cr	2.44	5.29	0.41	0.18	0.42	
	A2	3.42	14.55	0.41	0.28	0.30	
02	Bi	3.02	18.81	0.68	0.05	0.27	
F3	C1	3.94	18.25	0.98	0.01	0.01	
	Cr	4.70	16.94	-	-	-	
	A2	2.52	10.8	0.38	0.02	0.61	
D4	Ae	2.30	11.96	0.30	0.02	0.68	
F4	Bt1	2.25	11.06	0.50	0.05	0.45	
	BC	2.23	11.42	0.30	0.04	0.67	
	A2	2.65	6.99	0.51	-	0.56	
P5	Bi	2.58	8.21	0.50	0.04	0.46	
	C2	2.67	2.62	0.24	0.07	0.69	

- not detected.

contribution of expandable 2:1 clay minerals in this soil. These results are similar to those obtained by Ferreira (2013) for soils derived from basalt and rocks from the Lages Alkaline Complex. Further details of mineralogical analyses are discussed below.

Regarding the Fe_2O_3 contents of ADFE, the results indicate hypoferric soils for P1 and P2. Likewise, for hypoferric P3 and mesoferric P4 and P5, according to the criteria established by Santos et al. (2018).

Based on the set of observed characteristics, the superficial diagnostic horizon of the soils corresponding to profiles P1 and P2 were identified as prominent A that of profiles P4 and P5 as humic and that of P3 as chernozemic A. The subsurface diagnostic horizon of the P1, P2, P3, and P5 profiles was identified as incipient B, while that of the P4 profile as a nitic B horizon. Based on the other diagnostic attributes, the profiles were classified respectively, according to SiBCS (Santos et al., 2018) and Soil Taxonomy (Soil Survey Staff, 2014) as: Cambissolo Háplico Aluminico típico (Humudepts) (P1 and P2 profile), Nitossolo Bruno Distrófico húmico (Kandiudox) (P4 profile), and Cambissolo Húmico Alumínico típico (Humudepts) (P5 profile).

Mineralogical characteristics of the clay fraction of the studied profiles

Profile 1 – Nepheline Syenite

In the typical Cambissolo Háplico Aluminico típico (Humudepts), developed from nepheline syenite, the horizon diffractograms indicate similar mineralogy along with the profile, composed of kaolinite, with probable 2:1 layer interstratification, expandable 2:1 clay minerals, and micas and/or illites, variations occur mainly in the proportions of expandable 2:1 layer clay minerals (Figure 2A and 2B).

The dominant mineral in this soil is kaolinite, identified by its most intense reflections at 0.720 and 0.357 nm, followed by the least intense at 0.237 nm, in magnesium samples (Mg 25), whose main reflection area (001) was greater than that of the other minerals individually, being confirmed by their disappearance in the sample saturated with K and heated to 550 °C (Dixon, 1989). The base of these reflections is wide, and the peaks are asymmetrical towards the lowest 20 angles, in the case of the reflection of the 001 plane, and towards higher angles in the case of the 002, indicative of minerals with low structural order, of low crystallinity (Aparicio & Galán, 1999). The asymmetry in the 0.720 and 0.357nm peaks can also indicate the interstratification of 2:1 layers in the kaolinite crystals (Bortoluzzi et al., 2007). Nevertheless, it was not possible to identify whether it was a kaolinite-smectite (KS) or another interstratified.

Reflections around 1.47 nm in samples saturated with Mg at 25 °C, which did not undergo expansion with ETG (ethylene glycol), indicated the possibility of smectite or vermiculite (Barnhisel & Bertsch, 1989). However, in samples saturated with K, the layers do not undergo complete contraction at 10 Å after heating to 350 degrees (K 350), maintaining a reflection



Figure 2. Diffractograms of the clay fraction of profiles P1 (A and B), P2 (C and D), P3 (E and F), P4 (G and H), and P5 (I and J), with magnesium at 25 °C (Mg) and Mg plus ethylene glycol (Mg+EG), and with potassium at 25 °C (K25), 100 °C (K100), 350 °C (K350), and 550 °C (K550) for selected horizons.

with a value close to 1.25 nm, revealing that they are 2:1 layer clay minerals with hydroxy-Al polymers in the interlayers, probably vermiculites (VHE) (Barnhisel & Bertsch, 1989). Such minerals have been frequently found in the clay fraction of soils in the region of Lages (Almeida et al. 2018; 2019).

Micas and/or illites are of low expression, confirmed by reflections of 1.012, 0.500, and 0.334 nm. This pattern is maintained along with the profile but with lower intensity of kaolinite and illite reflections on the B and C1 horizons. The reflections around 0.415 and 0.417 nm indicate the presence of goethite, responsible for the predominant brownish color in the soil.

The still expressive presence of 2:1HE layer clay minerals also reveal the occurrence of partial bissilization processes, probably occurred in a drier past climate, which in the current wetter and colder climate, suffered intercalation with hydroxy-Al polymers in the interlayers, making them more thermodynamically stable (Karatahanasis et al., 1983), and so they are still preserved in the soil. The mineralogical composition observed is compatible with the clay activity values (Table 2) and with the Ki index, slightly higher than 2.2.

Profile 2 – Volcanic Breccia

In table 3, it is observed that the area of the reflections around 1.4 nm decreases from the base to the top of the profile, indicating their alteration with the advance of the weathering towards the surface (data not shown). Concomitantly, there was a relative increase in micas (or illites) in the same direction, without significantly altering the kaolinite contents.

Kaolinite and micas (or illites) are the predominant minerals in most horizons, except for Cr, in which kaolinites are found in proportions similar to minerals with peaks at 1.4 nm (Table 3).

In all horizons, kaolinite reflections are narrow and acute at the top. However, they present asymmetry (and greater width) in the median and inferior portions, suggesting the presence of interstratified 2:1 layer kaolinite-clay minerals in association with pure kaolinites (Figure 2C and 2D). The disappearance of kaolinite reflections when the samples were heated to 550 °C confirmed their identification (Dixon, 1989; Testoni et al., 2017; Almeida et al., 2019).

Intense reflections identified mica and/or illites at 1.003, 0.499, and 0.333 nm, with greater intensity in the A2 (data not shown) and BAi horizons, in the samples saturated with Mg at 25°C (Figure 2C). In the heating treatments, a better expression of the 0.999 nm reflections was observed due to the contraction of the layers of the expandable minerals. Clay minerals with peaks around 1.4 nm decreased towards the surface, not suffering a substantial change in the position of their reflections in samples with ethylene glycol. However, they suffered partial contraction to values around 1.25 nm in treatments with K at 350 °C, revealing that it is an expandable mineral, identified as vermiculite with interlayer hydroxy-Al polymers (VHE) (Barnhisel & Bertsch, 1989; Testoni et al., 2017; Almeida et al., 2019).

Profile 3 – Kimberlite Breccia

Profile 3, developed from the kimberlite breccia and classified as a Chernossolo Háplico Órtico típico (Hapludolls), showed a dominance of 2:1 clay minerals in all horizons, followed by kaolinites and micas, as indicated by the relative areas of the various minerals in table 3.

In Table 3 and Figure 2F, it is observed that in the Cr horizon, practically only a mineral with a reflection around 1.55 nm was detected; in the sample saturated with Mg at 25 °C, their amounts are reduced by more than half at the most superficial horizon. On the other hand, from the bottom to the top, the proportions of minerals with reflections increase around 1.0 nm (micas) and 0.72 nm (kaolinites). Such behavior seems to indicate that minerals with peaks of 1.55 nm were largely altered by weathering in the more superficial horizons, forming kaolinites, as well as allowing the expression of the mica peaks, more resistant to weathering, by a relative increase in their quantities.

After being solvated with ETG, the 2:1 layers underwent a slight expansion, either forming reflections at 2θ lower angles, as in Cr and C1, or forming a plateau in the other horizons, they all indicated the presence of an expandable mineral. Considering that, in this soil, the presence of phlogopite macrocrystals was identified in expressive proportions in the coarser fractions, this suggests the hypothesis of the presence of vermiculites in the clay fraction since these, in most cases, are formed from the alteration of micas (Douglas, 1989). For the formation of vermiculite, Mg comes from the weathering of minerals from the olivine and pyroxene groups present in the matrix rock. Although most vermiculites in soils do not expand in solvation treatments, Douglas (1989) refers to the occurrence of low-charge trioctahedral micas, which after saturated with Mg and treated with ETG, may undergo slight expansion to spacings around 1.55 to 1.6 nm, which occurred in the samples studied, mainly in the last two horizons. Ferreira (2013) found a similar mineralogical composition in Chernosol derived from olivine melilithite from the Lages Plateau.

In the heating treatments of samples saturated with potassium (Figure 2E and 2F), it is observed that there was a gradual collapse of the layers in all horizons, with a spacing reduction to positions around 1.25 or 1.0 nm. This situation confirms the presence of vermiculites with or without interlayer hydroxy polymers (Douglas, 1989; Almeida et al., 2019). Reflections around 1.0, 0.49, and 0.33 nm confirm the presence of micas, and/or illites, better visualized only in the first two horizons.

Kaolinite, which occurs in a smaller proportion, increases from the base to the top of the profile (Figure 2E and 2F) and is already detected in low quantities in the C1 horizon. In addition, quartz (narrow and acute reflection around 0.334 nm at the two most superficial horizons) and goethite (reflection around 0.415 nm) were also identified in this profile.

The presence of high amounts of vermiculites in the closest horizons of the rock, as well as their still expressive presence in the more superficial ones, are therefore compatible with the relatively high activity values of the clay fraction in this soil (Table 2), as well as with the Ki index, which was above 3.0 in most horizons. On the other hand, the mentions of trioctahedral vermiculites in Brazilian soils are rare. In acidic soils, under intense weathering, mica is directly transformed to VHE without going through the transformation step into vermiculite (Kampf & Curi, 2012).

Profile 4 - Phonolitic Tephrite

Profile 4, formed from the Phonolitic Tephrite rock and classified as Nitossolo Bruno Distrófico húmico (Kandiudox), has similar mineralogy in all analyzed horizons. Kaolinite was the dominant clay mineral, except for Bt1, where there was a predominance of clay minerals with spacing around 1.4 nm (Figure 2G, Table 3). Micas (or illites) were also identified in all horizons in small quantities (Table 3). In even smaller quantities, other minerals present were gibbsite (reflection at 0.48 nm) and goethite (reflection at 0.415 nm).

Minerals with reflections around 1.4 nm show a very similar pattern along the horizons (Figure 2G and 2H), despite the semiquantitative differences estimated by the ratio of areas of the main reflections (Table 3). The main reflections present asymmetries towards the greater angles (between 1.4 and 1.0 nm), clearly indicating the occurrence of expansive 2:1 mica-clay mineral type interstratified in association with the last mentioned ones. There was no substantial change in the position of the 1.4 nm reflections with ETG treatment. In addition, there was a partial contraction of the layers when the potassium samples were heated to 350 °C, whose peaks were between 1.23 and 1.28 nm. Therefore, they were interpreted as indicative of the presence of VHE in association with interstratified Mica-VHE (Barnhisel & Bertsch, 1989; Almeida et al., 2019).

The micas (or illites), in low proportions in the samples, were identified by reflections around 1.0, 0.5, and 0.33 nm, whose quantities, estimated by the area ratio of clay minerals, increase from the base to the top of the profile (Table 3).

Kaolinites have broad reflections at 0.710, 0.355 nm, and 0.237 nm. They have a slight asymmetry at their base, indicative of the small size of the crystals of this mineral, with the probable structural disorder (Aparicio & Galán, 1999). Its identification is confirmed by the disappearance of the three reflections mentioned in the heating treatment of samples with potassium at 550 °C (Figure 2G) (Dixon, 1989; Testoni et al., 2017; Almeida et al., 2019).

The fourth mineral present is gibbsite, represented by low-intensity reflections in samples saturated with Mg, around 0.48 nm, and confirmed by their disappearance when subjected to heating at 350 °C in potassium treatments (Hsu, 1989). Current environmental conditions do not favor the formation of this mineral due to the anti-gibbsitic effect provided by the presence of high organic matter contents and the intercalation of amorphous polymers in the interlayers of the 2:1 clay minerals. Therefore, its presence in this soil may be related to local microsites in the rock, where the silica leaching processes may have been more intense (Kampf & Curi, 2012). Peaks with values at 0.415 nm indicate the presence of goethite, an oxyhydroxide responsible for the predominantly brown colors of the soil.

Profile 5 - Phonolite

In profile 5, which originated from the phonolite and classified as a Cambissolo Húmico Alumínico típico (Humudepts), the mineralogy was similar in all horizons, composed mainly of kaolinite and clay minerals of 2:1 layer, with peaks around 1.4 nm and less expressive amounts of micas and/or illites.

From the base to the top of the profile, an increase in clay minerals with reflections of 1.4 nm is observed (Table 3). In samples with Mg, there is a slight asymmetry towards the greater angles, suggesting the presence of expandable 2:1 layer mica-clay mineral interstratified. There was no change in the position of the reflections due to glycolation, but particularly in the C2 horizon, heating the samples with K to 350 °C causes the layers to contract almost completely, a behavior similar to that of vermiculites, with low intercalation of hydroxy-Al polymers between layers. In the A2 and Bi horizons, there is also no expansion of the layers with the ETG treatment. However, heating to 350 °C does not cause a complete collapse of the layers, maintaining a small reflection in the spacing around 1.1 to 1.3 nm, thus revealing that it is VHE. This behavior indicates that, closer to the rock, the conditions were favorable to the formation of purer vermiculites. At the same time, in the more superficial horizons, due to the intensification of the weathering and leaching processes of the bases, the greater amount of Al favors its intercalation in the interlayer spaces, forming more VHE.

Kaolinite, present in all horizons in relatively similar proportions (intense reflections at 0.712, 0.356, and 0.237 nm) (Figure 2I), is confirmed by the disappearance of these reflections in heating treatments at 550 °C.

The amounts of micas or illites decrease from the base to the top of the profile (Table 3), probably due to their gradual transformation into VHE or their destruction by weathering, forming kaolinites. There is also gibbsite in small quantities, with reflections at 0.483 nm and quartz, with reflections at 0.424 and 0.333.

Relationship between mineralogy, chemical properties, and soil genesis

In practically all profiles, the marked influence of the chemical and mineralogical composition of the matrix rock in the genesis of the soils was evidenced, where those with higher contents of CaO and MgO, and lower contents of SiO2 (Kimberlite Breccia and Phonolithic Tephrite), tended to form soils with higher pH values, higher base content, and lower exchangeable aluminum contents.

Goethite was the only iron oxyhydroxide detected in soils, being responsible for their brownish colors. The wet and cold environment of the Lages Plateau, associated with high levels of organic matter (Almeida et al., 2019), the longer average residence time of water in the soil, causing slower oxidation of iron, favored the formation of goethite, as widely reported in similar environments (Schwertmann, 1985).

In profiles P1 and P5 developed respectively from nepheline syenite and phonolite, the mineral constituents of these rocks, rich in feldspar and feldspathoid and poor in mafic minerals, suffered intense weathering in the wet and cold environment of the Lages Plateau, leading to the formation of Humudepts (Cambissolo Háplico ou Húmico), with acidic reaction, with low sum and base saturation and with high levels of exchangeable aluminum, even being soils with incipient development. Besides the dominance of kaolinite, there is expressive participation of VHE and interstratified. Despite having CEC and lower expansivity than their pure counterparts (Barnhisel & Bertsch, 1989), such clay minerals certainly contributed to the increase in negative charges, whose clay activity was greater than 20 cmol, kg⁻¹ in both cases.

The rock of the P2 profile (kimberlite breccia) presented low calcium and magnesium oxides content, standing out. However, for the high K₂O contents, surpassing 8%, the highest content among the studied rocks (Table 1). The chemical poverty in calcium and magnesium of this rock is the main cause of the very low content of these exchangeable cations in the Humudepts (Cambissolo Háplico) developed from it. The mineralogy of the clay fraction was similar to that of the nepheline syenite profile, composed of kaolinite with expressive proportions of VHE and illites, responsible for clay activity values also above 20 cmol_c kg⁻¹, a situation compatible with the Ki values, around 2.4. The soil appears to have been developed from the weathering alteration of the "in situ" substrate.

As for the P3 profile, the chemical composition of the rock revealed the highest content of Ca and Mg oxides among the studied rocks, as well as TiO₂, and the lowest content of Al₂O₃ (Table 1). The Hapludolls (Chernossolo Háplico) developed from this rock, resulting from the alteration of the in-situ rock, of eutroferric character, was the only soil that presented high natural fertility among the studied ones, with high contents of exchangeable Ca and Mg, absence of exchangeable Al, the activity of clay fraction greater than 33 cmol, kg⁻¹ and Ki values greater than 3.0. Furthermore, low-charge trioctahedral vermiculites were practically the only clay minerals present in the Cr horizon, which are still largely preserved in association with kaolinites in the more superficial horizons. These characteristics point to a very recent origin of this soil, whose rock richness in more easily weatherable primary minerals, such as olivines, pyroxenes, and phlogopites, contributed to preserving a soil with high natural fertility, despite the humid environment currently dominant in the Lages Plateau. Soil similar to the one studied was identified in a restricted area in Palmeira (SC), by Ferreira (2013), developed from the ultrabasic rock olivine melilithite.

The P4 profile Kandiudox (Nitossolo Bruno), developed from phonolitic tephrite, in pediment position, unlike the other soils developed on alkaline rocks (P1 and P5), which presented very low sum and base saturation and aluminum character, presented higher values for the two first attributes, notably in the more superficial horizons. Smaller amounts of exchangeable aluminum, pointing to a slight improvement in natural fertility. It showed similarities in the mineralogical composition with the soils corresponding to profiles P1, P2, and P5 (Kaolinites and VHE), but with the addition of Mica-VHE interstratified.

Conclusions

Profiles P1, P2, and P5 had similar chemical, physical, and mineralogical characteristics. They are clayey, acidic soils with kaolinite associated with vermiculite with hydroxy-Al interlayers (VHE) and smaller amounts of mica and/or illite.

The soil of the P4 profile, developed from the phonolitic tephrite, showed a significant improvement in chemical properties compared to that seen in the P1, P2, and P5 profiles. The mineralogical composition of this soil indicated kaolinite as the predominant mineral, VHE, and mica-VHE interstratified, with small amounts of gibbsite.

The P3 profile, unlike the others, showed chemical properties indicating more fertile soil. In addition, the mineralogical composition of this profile showed a predominance of trioctahedral vermiculites in the clay fraction.

Soils P1 and P2 were classified as typical Cambissolo Háplico Alumínico típico, P3 as Chernossolo Háplico Órtico típico, P4 as Nitossolo Bruno Distrófico húmico, and P5 as Cambissolo Húmico Aluminico típico.

Compliance with Ethical Standards

Author contributions: Conceptualization: AEDVL, JAA; Data curation: AEDVL, JAA; Formal analysis: AEDVL, JAA; Funding acquisition: JAA; Investigation: AEDVL, JAA; Methodology: AEDVL, JAA; Project administration: JAA; Resources: AEDVL, JAA; GOMC; CJRL; Software: AEDVL; Supervision: JAA; Validation: AEDVL, JAA; GOMC; CJRL; Visualization: GOMC; CJRL; Writing – original draft: AEDVL, GOMC; CJRL; Writing – review & editing: AEDVL, GOMC; CJRL.

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